VERIFICATION OF TRANSLATION

I, Yasuo Yasutomi of Chuo BLDG., 4-20, Nishinakajima 5-chome, Yodogawa-ku, Osaka-shi, Osaka 532-0011 JAPAN, hereby declare that I am conversant with the Japanese and English languages and that I am the translator of the documents attached and certify that to the best of my knowledge and belief the following is a true and correct English translation of the Japanese Patent Application No. Hei 10-285797 in the name of KANEKA CORPORATION.

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[Title of the Invention] CURABLE COMPOSITION
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[Document Name] Description
[Title of the Invention]
[Scope of Claims for Patent]
[Claim 1] A curable composition comprising the following two components:
(A) a vinyl polymer having at least one crosslinking silyl group of the general formula (1) per molecule:

$$-[Si(R^1)_{2-b}(Y)_bO]_m-Si(R^2)_{3-a}(Y)_a \quad (1)$$

wherein R^1 and R^2 may be the same or different and each represents an alkyl group containing 1 to 20 carbon atoms, an aryl group containing 6 to 20 carbon atoms, an aralkyl group containing 7 to 20 carbon atoms, or a triorganosiloxy group of the formula $(R')_3SiO-$, where R' represents a univalent hydrocarbon group containing 1 to 20 carbon atoms and the plurality of R' groups may be the same or different, and when two or more R^1 or R^2 groups are present, the plurality of groups may be the same or different; Y represents a hydroxyl group or a hydrolyzable group and, when two or more Y groups are present, they may be the same or different; a represents an integer of 0, 1, 2 or 3; b represents an integer of 0, 1 or 2; m is an integer of 0 to 19; with the condition that the relation of $a + mb \geq 1$ is satisfied and
(B) a high molecular plasticizer.
[Claim 2] The curable composition according to Claim 1, wherein the vinyl polymer (A) has a molecular weight distribution value of less than 1.8.
[Claim 3] The curable composition according to Claim 1 or 2, wherein the vinyl polymer (A) is a (meth)acrylic polymer.
[Claim 4] The curable composition according to any of Claims 1 to 3 wherein the vinyl polymer (A) is an acrylic polymer.
[Claim 5] The curable composition according to any of Claims 1 to 4 wherein the vinyl polymer (A) is producible by living radical polymerization technique.

[Claim 6] The curable composition according to any of Claim 1 to 5

wherein the vinyl polymer (A) is producible by atom transfer radical polymerization technique.

[Claim 7] The curable composition according to any of Claims 1 to 6

wherein the vinyl polymer (A) has at least one crosslinking silyl group of the general formula (1) at the molecular chain terminus per molecule.

[Claim 8] The curable composition according to any of Claims 1 to 7

wherein (A) the vinyl polymer having at least one crosslinking silyl group of the general formula (1) per molecule is obtainable by a process comprising

(1) a step of polymerizing a vinyl monomer using an organohalogen compound or a sulfonyl halide as the initiator and a transition metal complex as the catalyst by a radical polymerization technique to synthesize a halogen-terminated vinyl polymer,

(2) a step of reacting the halogen-terminated vinyl polymer obtained in said step (1) with an alkenyl group-containing oxyanion to effect substitution for the halogen and thereby synthesize an alkenyl-terminated vinyl polymer, and

(3) a step of adding a hydrosilane compound having a crosslinking silyl group represented by the general formula (1) to the terminal alkenyl group of the alkenyl-terminated vinyl polymer obtained in said step (2) to convert the terminal alkenyl group to a substituent containing said crosslinking silyl group.

[Claim 9] The curable composition according to any of Claims 1 to 7

wherein (A) the vinyl polymer having at least one crosslinking silyl group of the general formula (1) per molecule is obtainable by a process comprising

(1) a step of polymerizing a vinyl monomer by a living radical

polymerization technique to prepare a vinyl polymer,
(2) a step of reacting the vinyl polymer obtained in said step (1) with a compound having at least two sparingly polymerizable alkenyl groups to synthesize an alkenyl-terminated vinyl polymer, and
(3) a step of adding a hydrosilane compound having a crosslinking silyl group represented by the general formula (1) to the terminal alkenyl group of the alkenyl-terminated vinyl polymer obtained in said step (2) to convert the terminal alkenyl group to a substituent containing said crosslinking silyl group.

[Claim 10] The curable composition according to Claim 1

wherein the high molecular plasticizer (B) has a number average molecular weight of 800 to 10000.

[Claim 11] The curable composition according to any of Claims 1 to 10

wherein the high molecular plasticizer (B) is a vinyl polymer.

[Claim 12] The curable composition according to Claim 10 or 11

wherein the high molecular plasticizer (B) has a molecular weight distribution value of less than 1.8.

[Claim 13] The curable composition according to any of Claims 1 or 10 to 12

wherein the high molecular plasticizer (B) is producible by living radical polymerization technique.

[Claim 14] The curable composition according any of Claims 1 or 10 to 13

wherein the high molecular plasticizer (B) is producible by atom transfer radical polymerization technique.

[Detailed Description of the Invention]

[0001]

[Technical Field of the Invention]

The present invention relates to a curable composition. More particularly, the invention relates to a curable composition comprising a vinyl polymer having a crosslinking

silyl group and a high molecular plasticizer.

[0002]

[Prior Art]

A vinyl polymer having at least one crosslinking silicon-containing group (hereinafter referred to sometimes as "crosslinking silyl group") comprising a hydroxyl or hydrolyzable group bound to a silicon atom and capable of siloxane bonding or a cured product obtainable from this has excellent heat resistance and weather resistance, therefore it can be used in various fields such as sealants, coatings, sealing materials or members and so on.

[0003]

[Subject which the Invention is to Solve]

The cured products obtainable by using a vinyl polymer having at least one crosslinking silyl group as the curable component exhibit good coatability when a coating is applied thereon. However, when a coating known as "alkyd coating" is applied, the coating is hard to be dried and cures easily.

[0004]

[Means for Solving the Problems]

In accordance with the above-mentioned state of the art, the present inventors found that the coatability of an alkyd coating to the cured product comprising a vinyl polymer having at least one crosslinking silyl group can be improved, thus they completed the present invention.

[0005]

That is, the present invention relates to a curable composition comprising the following two components:

(A) a vinyl polymer having at least one crosslinking silyl group of the general formula (1) per molecule:

$$-[Si(R^1)_{2-b}(Y)_bO]_m-Si(R^2)_{3-a}(Y)_a \qquad (1)$$

wherein R^1 and R^2 may be the same or different and each represents an alkyl group containing 1 to 20 carbon atoms, an aryl group containing 6 to 20 carbon atoms, an aralkyl group containing 7 to 20 carbon atoms, or a triorganosiloxy group of the formula

$(R')_3SiO-$, where R' represents a univalent hydrocarbon group containing 1 to 20 carbon atoms and the plurality of R' groups may be the same or different, and when two or more R^1 or R^2 groups are present, the plurality of groups may be the same or different; Y represents a hydroxyl group or a hydrolyzable group and, when two or more Y groups are present, they may be the same or different; a represents an integer of 0, 1, 2 or 3; b represents an integer of 0, 1 or 2; m is an integer of 0 to 19; with the condition that the relation of $a + mb \geq 1$ is satisfied and

(B) a high molecular plasticizer.

[0006]

[Embodiment of the Invention]

The curable composition of the present invention comprises the above (A) component vinyl polymer and (B) component high molecular plasticizer.

[0007]

In the following, the curable composition of the invention is described in detail.

[(A) vinyl polymer]

The vinyl polymer having at least one crosslinking silyl group of the above general formula (1), for use as (A) component, crosslinks by siloxane bonding.

[0008]

In the above general formula (1), R^1 and R^2 may be the same or different and each represents an alkyl group containing 1 to 20 carbon atoms, an aryl group containing 6 to 20 carbon atoms, an aralkyl group containing 7 to 20 carbon atoms, or a triorganosiloxy group of the formula $(R')_3SiO-$. R' represents a univalent hydrocarbon group containing 1 to 20 carbon atoms and the plurality of R' groups may be the same or different, and when two or more R^1 or R^2 groups are present, they may be the same or different.

[0009]

In the above general formula (1), Y represents a hydroxyl

group or a hydrolyzable group and, when two or more Y groups are respectively present, they may be the same or different. The total number of Y is preferably within the range of 1 to 5.

[0010]

The hydrolyzable group is not particularly restricted and there may be mentioned, for example, hydrogen or halogen atom, alkoxy, acyloxy, ketoximato, amino, amido, aminoxy, mercapto and alkenyloxy groups, and the like. Among these, alkoxy groups are preferred for assuring hydrolyzability under mild conditions and ease of handling.

[0011]

In the above general formula (1), a represents an integer of 0, 1, 2 or 3; b represents an integer of 0, 1 or 2; and m is an integer. Y can be bound to one silicon atom within the range of 1 to 3. a, b and m satisfy the relation of $a + mb \geq 1$. That is, at least one Y is contained in the above general formula (1).

[0012]

The silicon atom constituting the above crosslinking silyl group may be present in one, or two or more of them may also be present. When the silicon atom is bound to a siloxane bonding, the number thereof may be up to about 20, thus m is preferably 0 to 19.

[0013]

The monomer constituting the main chain of said vinyl polymer having at least one crosslinking silyl group is not particularly restricted provided that it is a vinyl monomer. For example, there may be mentioned (meth)acrylic monomers such as (meth)acrylic acid, methyl (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth)acrylate, isopropyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, tert-butyl (meth)acrylate, n-pentyl (meth)acrylate, n-hexyl (meth)acrylate, cyclohexyl (meth)acrylate, n-heptyl (meth)acrylate, n-octyl

(meth)acrylate, 2-ethylhexyl (meth)acrylate, nonyl (meth)acrylate, decyl (meth)acrylate, dodecyl (meth)acrylate, phenyl (meth)acrylate, toluyl (meth)acrylate, benzyl (meth)acrylate, 2-methoxyethyl (meth)acrylate, 3-methoxypropyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, stearyl (meth)acrylate, glycidyl (meth)acrylate, 2-aminoethyl (meth)acrylate, gamma -(methacryloyloxypropyl)trimethoxysilane, gamma -(methacryloyloxypropyl)methyldimethoxysilane, (meth)acrylic acid-ethylene oxide adducts, trifluoromethylmethyl (meth)acrylate, 2-trifluoromethylethyl (meth)acrylate, 2-perfluoroethylethyl (meth)acrylate, 2-perfluoroethyl-2-perfluorobutylethyl (meth)acrylate, 2-perfluoroethyl (meth)acrylate, perfluoromethyl (meth)acrylate, diperfluoromethylmethyl (meth)acrylate, 2-perfluoromethyl-2-perfluoroethylmethyl (meth)acrylate, 2-perfluorohexylethyl (meth)acrylate, 2-perfluorodecylethyl (meth)acrylate and 2-perfluorohexadecylethyl (meth)acrylate; styrenic monomers such as styrene, vinyltoluene, alpha -methylstyrene, chlorostyrene, and styrenesulfonic acid and salts thereof; fluorinecontaining vinyl monomers such as perfluoroethylene, perfluoropropylene and vinylidene fluoride; silicon-containing vinyl monomers such as vinyltrimethoxysilane and vinyltriethoxysilane; maleic anhydride, maleic acid and monoalkyl esters and dialkyl esters of maleic acid; fumaric acid and monoalkyl esters and dialkyl esters of fumaric acid; maleimide monomers such as maleimide, methylmaleimide, ethylmaleimide, propylmaleimide, butylmaleimide, hexylmaleimide, octylmaleimide, dodecylmaleimide, stearylmaleimide, phenylmaleimide and cyclohexylmaleimide; nitrile-containing vinyl monomers such as acrylonitrile and methacrylonitrile; amido-containing vinyl monomers such as acrylamide and methacrylamide; vinyl esters such as vinyl acetate, vinyl propionate, vinyl pivalate,

vinyl benzoate and vinyl cinnamate; alkenes such as ethylene and propylene; conjugated dienes such as butadiene and isoprene; vinyl chloride, vinylidene chloride, allyl chloride, allyl alcohol and so forth.

[0014]

These may be used singly or two or more of them may be used in combination.

[0015]

In the nomenclature used above, (meth)acrylic acid, for instance, means acrylic acid and/or methacrylic acid. Hereinafter, the same shall apply.

From the standpoint of physical properties, the vinyl polymer having at least one of the above crosslinking silyl groups is preferably a (meth)acrylic polymer synthesized by using a (meth)acrylic monomer, among said various monomers, in a proportion of not less than 40 weight %. The still more preferred is an acrylic polymer synthesized by using an acrylic monomer, among said various monomers, in a proportion of not less than 30 weight %.

[0016]

The molecular weight of the vinyl polymer having at least one of said crosslinking silyl groups is not particularly restricted but is preferably within the range of 500 to 100000. At a molecular weight less than 500, the intrinsic characteristics of a vinyl polymer are hardly manifested and, at above 100000, handling may become difficult in some instances.

[0017]

The molecular weight distribution, namely the ratio (Mw/Mn) of weight average molecular weight (Mw) to number average molecular weight (Mn) , of the vinyl polymer having at least one of said crosslinking silyl groups is not particularly restricted. For facilitating handling by controlling the viscosity of the curable composition at a sufficiently low amount while securing necessary cured physical properties,

however, a narrow molecular weight distribution is preferred. The molecular weight distribution value is preferably less than 1.8, more preferably not more than 1.7, still more preferably not more than 1.6, yet more preferably not more than 1.5, still more preferably not more than 1.4, most preferably not more than 1.3. The molecular weight distribution is most prevalently determined by gel permeation chromatography (GPC). The number average molecular weight and so on can be determined on the polystyrene equivalent basis using chloroform or THF as the mobile phase and polystyrene gel columns as columns.

[0018]

The method of synthesizing a vinyl polymer having at least one of said crosslinking silyl groups is not particularly restricted but includes various methods. However, from the standpoint of monomer universality and ease of control, the radical polymerization technique for introducing a crosslinking silyl group directly into the main chain and the technique which comprises synthesizing a vinyl polymer having a given functional group capable of converting to a crosslinking silyl group in one or more reaction steps and converting the given functional group to the crosslinking silyl group are preferred.

[0019]

The radical polymerization method which is used in the method for synthesizing a vinyl polymer having a given functional group including a crosslinking silyl group can be divided into the "general radical polymerization method" in which a monomer having a given functional group is simply copolymerized with a vinyl monomer using an azo or peroxide compound as the polymerization initiator and the "controlled radical polymerization method" which is capable of introducing a given functional group into a defined position such as the molecular chain terminus.

[0020]

The "general radical polymerization method" is an

expedient method and can be used in the practice of the present invention. However, by this method, a monomer having a given functional group is introduced into the product polymer only in probabilities. Therefore, in order to synthesize a polymer of high functionality, this monomer must be used in a fairly large amount, and thus there is a disadvantage that the controlled range of the properties becomes narrow. When conversely the amount of the monomer having a given functional group is small, the ratio of polymer molecules not provided with the given functional group is increased. Another disadvantage is that since the reaction is a free radical polymerization reaction, the molecular weight distribution is so broadened that only a polymer having a high viscosity can be obtained.

[0021]

The "controlled radical polymerization method" can be divided into the "chain transfer agent technique" in which a vinyl polymer having a functional group at the molecular chain terminus is produced by carrying out the polymerization reaction using a chain transfer agent having a given functional group, and the "living radical polymerization technique" in which the polymerization proceeds with the growing chain terminus constantly growing without being interrupted by a termination reaction to give a polymer approximating the designed molecular weight.

[0022]

The "chain transfer agent technique" is capable of giving a polymer of high functionality as compared with the "general radical polymerization method", and can be used in the practice of the present invention. But a chain transfer agent having a given functional group must be used in a fairly large amount relative to the initiator, with the consequent disadvantage in economics inclusive of the cost of treatment involved. A further disadvantage of the technique is that because it is also a free radical polymerization method as is said "general radical polymerization method", there can be obtained only a polymer

having a broad molecular weight distribution and a high viscosity.

[0023]

Unlike the above polymerization technology, the "living radical polymerization technique" is advantageous in that despite its also being a method for radical polymerization reaction which is generally considered to be hardly controllable because of the high velocity polymerization and high tendency of termination by radical-radical coupling or the like, a termination reaction does not easily take place, thus giving a polymer with a narrow molecular weight distribution (Mw/Mn = about 1.1 to 1.5), and further in that the molecular weight can be freely controlled by adjusting the monomer-initiator charge ratio.

[0024]

Since "living radical polymerization" is thus capable of giving a polymer having a narrow molecular weight distribution and a low viscosity and enables introduction of a monomer having a given functional group in an almost designated position, it is a further preferred method for producing a vinyl polymer having said given functional group.

[0025]

In a narrow sense of the term, "living polymerization" means a polymerization in which the molecule grows with its growth termini being constantly activated. Generally, however, the term is used to broadly cover as well a pseudo-living polymerization reaction in which the polymer grows while molecules with an activated terminus and molecules with an inactivated terminus are in equilibrium, and the term as used in this specification also has the latter broad meaning.

The "living polymerization" is not particularly restricted provided that it is a radical polymerization within the scope of the above definition. Recently, the "living radical polymerization" has been studied in earnest by many research groups. By way of illustration, this technology

includes the method employing a cobalt porphyrin complex as described in J. Am. Chem. Soc., 116, 7943 (1994) ; the method using a radical rapping agent such as a nitroxide compound as described in Macromolecules, 27, 7228 (1994), and the atom transfer radical polymerization (ATRP) method using an organohalogen compound as the initiator and a transition metal complex as the catalyst.

[0026]

Among such variations of the "living radical polymerization method", the "atom transfer radical polymerization" method in which a vinyl monomer is polymerized using an organohalogen compound or a sulfonyl halide compound as the initiator and a transition metal complex as the catalyst is still more preferred for the production of said vinyl polymer having a given functional group because, in addition to the above-mentioned advantages of "living radical polymerization" it is capable of giving a polymer having a halogen atom or the like at its terminus, which is comparatively favorable for a functional group exchange reaction, and offers a broad freedom in the initiator and catalyst design. Regarding this atom transfer radical polymerization method, reference can be made to Matyjaszewski et al.: J. Am. Chem. Soc., 117, 5614 (1995), Macromolecules, 28, 7901 (1995), Science, 272, 866 (1996), WO 96/30421, WO 97/18247, Sawamoto et al.: Macromolecules, 28, 1721 (1995), among others.

[0027]

As an initiator to be used in the above "atom transfer radical polymerization", there may be mentioned an organohalogen compound, in particular an organohalogen compound having a highly reactive carbon-halogen bond, or a sulfonyl halide compound or the like. As the above-mentioned organohalogen compound having a highly reactive carbon-halogen bond, there may be mentioned a carbonyl compound having a halogen atom at the alpha position, or a compound having a halogen at the benzyl position. These may be used alone or two

or more of them may be used in combination.

The transition metal complex to be used as the catalyst in the above "atom transfer radical polymerization" is not particularly restricted and there may be mentioned, for example, transition complexes whose center metals belong to Group 7, 8, 9, 10 or 11 of the periodic table of the elements and, as more preferred species, complexes of zero-valence copper, univalent copper, bivalent ruthenium, bivalent iron or bivalent nickel. Copper complexes are particularly preferred. These may be used alone, or two or more of them may be used in combination.

[0028]

The above univalent copper compound is not particularly restricted, and for example, there may be mentioned cuprous chloride, cuprous bromide, cuprous iodide, cuprous cyanide, cuprous oxide and cuprous perchlorate. When a copper compound is used, a ligand, for example 2,2'-bipyridyl or a derivative thereof, 1,10-phenanthroline or a derivative thereof, or a polyamine such as tetramethylethylenediamine, pentamethyldiethylenetriamine or hexamethyltris (2-aminoethyl)amine, is added for improving catalytic activity.

[0029]

The tristriphenylphosphine complex of bivalent ruthenium chloride ($RuCl_2(PPh_3)_3$) is also suited for use as a catalyst. When a ruthenium compound is used as the catalyst, an aluminum alkoxide can be added as an activator. Further, the bistriphenylphosphine complex of bivalent iron ($FeCl_2(PPh_3)_2$), the bistriphenylphosphine complex of bivalent nickel ($NiCl_2(FPh_3)_2$) and the bistributylphosphine complex of bivalent nickel ($NiBr_2(PBu_3)_2$) are also suited as catalysts.

[0030]

The above polymerization reaction can be carried out in the absence of a solvent or in any of various solvent. The above solvent is not particularly restricted, and there may be mentioned, for example, hydrocarbon solvents such as benzene

and toluene; ether solvents such as diethyl ether and tetrahydrofuran; halogenated hydrocarbon solvents such as methylene chloride and chloroform; ketone solvents such. as acetone, methyl ethyl ketone and methyl isobutyl ketone; alcohol solvents such as methanol, ethanol, propanol, isopropyl alcohol, n-butyl alcohol and tert-butyl alcohol; nitrile solvents such as acetonitrile, propionitrile and benzonitrile; ester solvents such as ethyl acetate and butyl acetate; carbonate solvents such as ethylene carbonate and propylene carbonate; and so on. These may be used singly or two or more of them may be used in admixture.

[0031]

The above "atom transfer radical polymerization" can be carried out within the temperature range of 0°c to 200°c, preferably within the range of room temperature to 150°c.

Next, the vinyl polymer having at least one crosslinking silyl group represented by the above general formula (1) is described in detail by means of specific examples in the following methods [A] to [E], but these are not any limitation.

[A] The method which comprises adding a hydrosilane compound having a crosslinking silyl group to a vinyl polymer having at least one alkenyl group in the presence of a hydrosilylation catalyst.

[B] The method which comprises reacting a vinyl polymer having at least one hydroxyl group with a compound having both a crosslinking silyl group and a functional group capable of reacting with the hydroxyl group, for example an isocyanato group.

[C] The method which comprises subjecting to reaction of a compound having both a polymerizable alkenyl group and a crosslinking silyl group, together with a predetermined vinyl monomer, in synthesizing a vinyl polymer by radical polymerization.

[D] The method which comprises subjecting a vinyl monomer to radical polymerization using a crosslinking silyl

group-containing chain transfer agent.

[E] The method which comprises reacting a vinyl polymer having at least one highly reactive carbon-halogen bond with a stable, crosslinking silyl group-containing carbanion.

[0032]

The method of producing the vinyl polymer having at least one alkenyl group which is to be used in the above production method [A] includes but is not limited to the following methods [A-a] to [A-j].

[0033]

[A-a] The method which comprises subjecting a compound having a polymerizable alkenyl group and a sparingly polymerizable alkenyl group, e.g. a compound of the general formula (2), together with a predetermined vinyl monomer, to reaction in synthesizing a vinyl polymer by radical, polymerization.

$H_2C=C(R^3)-R^4-R^5-C(R^6)=CH_2$ (2)

wherein R^3 represents a hydrogen atom or methyl group; R^4 represents -C(O)O- or an o-, m- or p-phenylene group; R^5 represents a direct bond or a C1-20 bivalent organic group which may optionally contain one or more ether linkages; R^6 represents a hydrogen atom, a C1-10 alkyl group, C6-10 aryl group or C7-10 aralkyl group.

[0034]

The timing of reacting said compound having both a polymerizable alkenyl group and a sparingly polymerizable alkenyl group is not particularly restricted but, when rubber-like properties are expected of the obtained crosslinked product, this compound is preferably reacted, as a second monomer, at a terminal stage of polymerization or after completion of the reaction of the vinyl monomer.

[0035]

[A-b] The method in which, in synthesizing a vinyl polymer by living radical polymerization, a compound having at least 2 sparingly polymerizable alkenyl groups, such as 1,5-hexadiene, 1,7-octadiene or 1,9-decadiene, is reacted at a terminal stage

of polymerization or after completion of the reaction of the vinyl monomer.

[0036]

The following methods [A-c] SIMILAR [A-f] can be used for producing a vinyl polymer having at least one alkenyl group from a vinyl polymer having at least one highly reactive carbon-halogen bond. The above polymer having at least one highly reactive carbon-halogen bond can be prepared by the processes [E-a] and [E-b] to be described hereinafter.

[0037]

[A-c] The method which comprises reacting a vinyl polymer having at least one highly reactive carbon-halogen bond with an organometal compound having an alkenyl group, typically represented by organotin compounds such as allyltributyltin, allyltrioctyltin, etc., to substitute an alkenyl-containing substituent for the halogen.

[0038]

[A-d] The method which comprises reacting a vinyl polymer having at least one highly reactive carbon-halogen bond with a stabilized carbanion having an alkenyl group, which may for example be represented by the general formula (3), to substitute an alkenyl group for the halogen.

$M^+C^-(R^7)(R^8)-R^9-C(R^6)=CH_2$ (3)

wherein R^6 is as defined above. R^7 and R^8 are electron-withdrawing groups for stabilizing carbanion C^-, or one is the above electron-withdrawing group and the other is hydrogen or C1-10 alkyl group or a phenyl group. R^9 is a direct bond or C1-10 divalent organic group which may contain one or more ether linkages. M^+ is an alkali metal ion, or a quaternary ammonium ion. As the electron-withdrawing groups of R^7 and R^8, $-CO_2R$, $-C(O)R$ and $-CN$ are preferred. Herein, R represents or C1-10 alkyl group, C6-10 aryl group, or C7-10 aralkyl group.

[0039]

[A-e] The method which comprises permitting an elemental metal, e.g. zinc, or an organometal compound to act upon a vinyl polymer

having at least one highly reactive carbon-halogen bond to prepare an enolate anion and, then, reacting it with an electrophilic compound having an alkenyl group, such as an alkenyl-containing compound having a leaving group, e.g. halogen or acetyl, a carbonyl compound having an alkenyl group, an isocyanate compound having an alkenyl group or an acid halide having an alkenyl group.

[0040]

[A-f] The method which comprises reacting a vinyl polymer having at least one highly reactive carbon-halogen bond with an alkenyl-containing oxyanion, such as the one represented by the general formula (4), or an alkenyl-containing carboxylate anion, such as the one represented by the general formula (5), to substitute an alkenyl-containing substituent for the halogen.

$H_2C{=}C(R^6)\text{-}R^{10}\text{-}O^-M^+$ (4)

(wherein R^6 and M^+ are as defined above; R^{10} represents a C1-20 bivalent organic group which may contain one or more ether linkages)

$H_2C{=}C(R^6)\text{-}R^{11}\text{-}C(O)O^-M^+$ (5)

(wherein R^6 and M^+ are as defined above; R^{11} represents a direct bond or a C1-20 bivalent organic group which may contain one or more ether linkages)

[0041]

The vinyl polymer having at least one alkenyl group can also be produced from a vinyl polymer having at least one hydroxyl group. The specific method is not particularly restricted but includes the following methods [A-g] to [A-j], among others. The starting vinyl polymer having at least one hydroxyl group can be prepared by the methods [B-a] to [B-i] to be described hereinafter.

[0042]

[A-g] The method which comprises permitting a base, such as sodium hydroxide, sodium methoxide, etc., to act on a vinyl polymer having at least one hydroxyl group and then reacting the same with an alkenyl-containing halide such as allyl

chloride;

[0043]

[A-h] The method which comprises reacting an alkenyl-containing isocyanate compound, such as allyl isocyanate or the like, with a vinyl polymer having at least one hydroxyl group;

[0044]

[A-i] The method which comprises reacting an alkenyl-containing acid halide, such as (meth)acryloyl chloride, with a vinyl polymer having at least one hydroxyl group in the presence of a base such as pyridine; and

[0045]

[A-j] The method which comprises reacting an alkenyl-containing carboxylic acid, such as acrylic acid, with a vinyl polymer having at least one hydroxyl group in the presence of an acid catalyst.

[0046]

Referring to the synthesis of said vinyl polymer having at least one alkenyl group, when a halogen is not directly involved in the introduction of the alkenyl group as in the methods [A-a] and [A-b], it is preferable to use the living radical polymerization technique. Between the above methods, the method [A-b] is preferred in view of the relative ease of control. Among variations of living radical polymerization, atom transfer radical polymerization is preferred.

[0047]

When an alkenyl group is to be introduced by converting the halogen group of a vinyl polymer having at least one highly reactive carbon-halogen bond as in the methods [A-c] to [A-f], it is preferable to use a vinyl polymer having at least one highly reactive terminal carbon-halogen bond as obtained by a radical polymerization (atom transfer radical polymerization) using an organohalogen compound or a sulfonyl halide as the initiator and a transition metal complex as the catalyst. More preferred is the method [A-f] in consideration of the ease of control.

[0048]

The hydrosilane compound having a crosslinking silyl group for use in the above synthetic method [A] is not particularly restricted but includes compounds represented by the following general formula (6), among others.

$H-[Si(R^1)_{2-b}(Y)_bO]_m-Si(R^2)_{3-a}(Y)_a$ (6)

wherein R^1, R^2, a, b, m and Y are as defined hereinbefore.

[0049]

Among these compounds, compounds of the following general formula (7) are preferred from availability points of view.

$H-Si(R^2)_{3-a}(Y)_a$ (7)

wherein R^2, Y and a are as defined above.

In adding said hydrosilane compound having a crosslinking silyl group to the alkenyl group of said polymer in said synthetic method [A], a transition metal complex catalyst is generally used as the hydrosilylation catalyst.

[0050]

The transition metal catalyst mentioned above is not particularly restricted but includes, among others, platinum metal and a dispersion of solid platinum in a matrix such as alumina, silica, carbon black or the like; chloroplatinic acid; a complex of chloroplatinic acid with an alcohol, aldehyde or ketone; platinum-olefin complexes and platinum(0)-divinyltetramethyldisiloxane complex; and compounds other than platinum compounds, such as $RhCl(FPh_3)_3$, $RhCl_3$, $RuCl_3$, $IrCl_3$, $FeCl_3$, $AlCl_3$, $PdCl_2.H_2O$, $NiCl_2$ and $TiCl_4$, among others. These catalysts can be used independently or two or more of them may be used in a combination of two or more thereof.

[0051]

The method of synthesizing said vinyl polymer having at least one hydroxyl group for use in the above synthetic method [B] and further in the above methods [A-g] to [A-j] is not particularly restricted but includes the following methods [B-a] to [B-i].

[0052]

[B-a] The method in which, in synthesizing a vinyl polymer by radical polymerization, a compound having both a polymerizable alkenyl group and a hydroxyl group, such as the compound represented by the following general formula (8), is reacted along with the predetermined vinyl monomer.

$H_2C=C(R^3)-R^4-R^5-OH$ (8)

(wherein R^3, R^4 and R^5 are as defined above)

[0053]

The timing of reacting said compound having both a polymerizable alkenyl group and a hydroxyl group is not particularly restricted but, when rubber-like properties are expected of the crosslinked product obtainable by. living radical polymerization, this compound is preferably reacted, as a second monomer, at a terminal stage of polymerization or after completion of the reaction of said predetermined vinyl monomer.

[0054]

[B-b] The method in which, in synthesizing a vinyl polymer by living radical polymerization, an alkenyl alcohol such as 10-undecenol, 5-hexenol or allyl alcohol is reacted at a terminal stage of polymerization or after completion of the reaction of the predetermined monomer.

[B-c] The method for radical polymerization of a vinyl monomer, as described in Japanese Kokai Publication Hei-5-262808, which comprises using a hydroxyl-containing chain transfer agent, such as a hydroxyl-containing polysulfide, in a large quantity.

[B-d] The method for radical polymerization of a vinyl monomer which comprises using hydrogen peroxide or a hydroxyl-containing initiator as described in Japanese Kokai Publication Hei-6-239912 and Japanese Kokai Publication Hei-8-283310, for instance.

[B-e] The method for radical polymerization of a vinyl monomer which comprises using an alcohol in excess as described in Japanese Kokai Publication Hei-6-116312.

[B-f] The method which comprises hydrolyzing the halogen of a

vinyl polymer containing at least one highly reactive. carbon-halogen bond or reacting it with a hydroxyl-containing compound to introduce a hydroxyl group into the polymer terminus as described in Japanese Kokai Publication Hei-4-132706.

[B-g] The method which comprises reacting a vinyl polymer having at least one highly reactive carbon-halogen bond with a hydroxyl-containing stabilized carbanion, such as the one represented by the following general formula (9), to substitute a hydroxyl-containing substituent for the halogen.

$M^{+}C^{-}(R^{7})(R^{8})-R^{9}-OH$ (9)

(wherein R^7, R^8 and R^9. are as defined above) . As the electron-withdrawing groups for R^7 and R^8, $-CO_2R$, $-C(O)R$ and $-CN$ are preferred. In the above formulas, R is as defined above.

[0055]

[B-h] The method which comprises permitting an elemental metal, e.g. zinc, or an organometal compound to act on a vinyl polymer having at least one highly reactive carbon-halogen bond to prepare an enolate anion and then reacting it with an aldehyde or a ketone.

[0056]

[B-i] The method which comprises reacting a vinyl polymer having at least one highly reactive carbon-halogen bond with a hydroxyl-containing oxyanion, such as the one represented by the general formula (10), or a hydroxyl-containing carboxylate anion, such as the one represented by the general formula (11), to substitute a hydroxyl-containing substituent for the halogen.

$HO-R^{10}-O^{-}M^{+}$ (10)

(wherein R^{10} and M^+ are both as defined above)

$HO-R^{11}-C(O)O^{-}M^{+}$ (11)

(wherein R^{11} and M^+ are both as defined above)

[0057]

Referring to the synthesis of said vinyl polymer having at least one hydroxyl group, when a halogen is not directly involved in the introduction of a hydroxyl group as in the above

methods [B-a] to [B-e], the living radical polymerization technique is preferred. In consideration of the ease of control, the method [B-b] is preferred. Among variations of living radical polymerization, atom transfer radical polymerization is preferred.

[0058]

When the halogen of a vinyl polymer having at least one highly reactive carbon-halogen bond is to be converted for the introduction of a hydroxy group as in the above methods [B-f] to [B-i], it is preferable to use a vinyl polymer having at least one highly reactive carbon-halogen bond at the terminus which has been obtained by the radical polymerization (atom transfer radical polymerization) using an organohalogen or suifonyl halide compound as the initiator and a transition metal complex as the catalyst. In consideration of the ease of control, the method [B-i] is still more preferred.

[0059]

The compound having both a crosslinking silyl group and an isocyanato or other functional group capable of reacting with a hydroxyl group which is to be used in the above production method [B] is not particularly restricted but includes, among others, gamma -isocyanatopropyltrimethoxysilane, gamma -isocyanatopropylmethyldimethoxysilane and gamma -isocyanatopropyltriethoxysilane. These may be used singly or two or more of them may be used combinedly.

[0060]

In carrying out the reaction according to the above production method [B], a urethane formation reaction catalyst known in the art may be used.

[0061]

The compound having both a polymerizable alkenyl group and a crosslinking silyl group to be used in the above production method [C] is not particularly restricted but includes, among others, compounds represented by the general formula (12) shown below, for example trimethoxysilylpropyl (meth)acrylate and

methyldimethoxysilylpropyl (meth) acrylate:

$H_2C=C(R^3)-R^4-R^{12}-[Si(R^1)_{2-b}(Y)_bO]_m-Si(R^2)_{3-a}(Y)_a$ (12)

wherein R^1, R^2, R^3, R^4, Y, a, b and m are as defined above; R^{12} represents a direct bond or a C1-20 bivalent organic group optionally containing one or more ether linkages. These may be used singly or two or more of them may be used in combination.

[0062]

In the above synthetic method [C], the timing of reacting said compound having both a polymerizable alkenyl group and a crosslinking silyl group is not particularly restricted but, when rubber-like properties are expected of the crosslinked product obtained by living radical polymerization, this compound is preferably reacted, as a second monomer, at a terminal stage of polymerization or after completion of the reaction of the predetermined vinyl monomer.

[0063]

The chain transfer agent having a crosslinking silyl group for use in the above synthetic method [D] is not particularly restricted but includes crosslinking silyl group-containing mercaptan compounds and hydrosilane compounds having a crosslinking silyl group as disclosed in Japanese Kokoku Publication Hei-3-14068 and Japanese Kokoku Publication Hei-4-55444, among others. Furthermore, in order to enhance the rate of introduction of the crosslinking silyl group, a radical initiator having the crosslinking silyl group can also be used in combination.

[0064]

The method of synthesizing the vinyl polymer having at least one highly reactive carbon-halogen bond for use in the above synthetic method [E] and further in the above methods [A-c] to [A-f] and [B-f] to [B-i] is not particularly restricted but includes the following processes [E-a] and [E-b].

[0065]

[E-a] A radical polymerization process which, as described in, inter alia, Japanese Kokai Publication Hei-4-132706, comprises

using a halogen compound, such as carbon tetrachloride, ethylene chloride, carbon tetrabromide, methylene bromide or the like, as the chain transfer agent (chain transfer agent technique).

[0066]

[E-b] An atom transfer radical polymerization process which comprises using an organohalogen compound or a sulfonyl halide compound as the initiator and a transition metal complex as the catalyst.

[0067]

The crosslinking silyl group-containing stabilized carbanion for use in the above synthetic method [E] is not particularly restricted but includes compounds represented by the following general formula (13), among others.

$M^+C^-(R^7)(R^8)-R^{13}-C(H)(R^{14})-CH_2-[Si(R^1)_{2-b}(Y)_bO]_m-Si(R^2)_{3-a}(Y)_a$ (13)

Wherein R^1, R^2, R^7, R^8, Y, a, b and m are as defined above. R^{13} is a direct bond or C1-10 divalent organic group which may contain one or more ether linkages. R^{14} represents hydrogen, C1-10 alkyl group, C6-10 aryl group, or C7-10 aralkyl group. As the electron-withdrawing groups of R^7 and R^8, $-CO_2R$, $-C(O)R$ and $-CN$ are preferred. Herein, R is as defined above.

When the curable composition according to the invention is foamed and cured to give a foam product which is required to have rubber-like properties in particular, it is preferable that at least one crosslinking silyl group is present at the molecular chain terminus, for the molecular mass between crosslinking points, which has considerable bearings on rubber elasticity, can then be large. More preferably, all crosslinking silyl groups are located at molecular chain termini.

The technology of producing a vinyl polymer having at least one crosslinking silyl group at the molecular chain terminus, particularly such a (meth)acrylic polymer, is described in, Japanese Kokoku Publication Hei-3-14068,

Japanese Kokoku Publication Hei-4-55444 and Japanese Kokai Publication Hei-6-211922. However, since these are invariably free radical polymerization processes utilizing said "chain transfer agent technique", the resulting polymer contains crosslinking silyl groups at molecular chain termini at a fairly high rate but has the drawback that the molecular weight distribution value, represented by Mw/Mn, is as large as 2 or more and, hence, the viscosity of the polymer is high. Therefore, in order to provide a vinyl polymer having a small molecular weight distribution value, hence a low viscosity value, and, yet, a high proportion of crosslinking silyl groups at molecular chain termini, the "living radical polymerization technique" mentioned hereinbefore is preferably employed.

[0068]

Therefore, the vinyl polymer having at least one hydroxyl, halogen or alkenyl group for use in synthesizing said vinyl polymer having at least one crosslinking silyl group preferably has such a functional group at a molecular chain terminus.

[0069]

To produce a vinyl polymer having at least one said crosslinking silyl group at the molecular chain terminus by the "atom transfer radical polymerization technique" which is the preferred variation of the "living radical polymerization" method, the initiator to be used is preferably an organohalogen or sulfonyl halide compound having two or more initiation points. The resulting vinyl polymer having at least one highly reactive carbon-halogen bond at the molecular chain terminus can be easily converted to the corresponding vinyl polymer having at least one Said crosslinking silyl group at the molecular chain terminus.

[0070]

An organohalogen or sulfonyl halide compound having two or more initiation sites is not particularly restricted but includes the following compounds, among others.

[0071]

As specific examples thereof, there may be mentioned; o-, m- or p-$XCH_2-C_6H_4-CH_2X$, o-, m- or p-$CH_3C(H)(X)-C_6H_4-C(H)(X)CH_3$, o-, m- or p-$(CH_3)_2C(X)-C_6H_4-C(X)(CH_3)_2$
(in the above formulae, C_6H_4 stands for a phenylene group; X represents a chlorine, bromine or iodine atom),
$RO_2C-C(H)(X)-(CH_2)_n-C(H)(X)-CO_2R$, $RO_2C-C(CH_3)(X)-(CH_2)_n-C(CH_3)(X)-CO_2R$, $RC(O)-C(H)(X)-(CH_2)_n-C(H)(X)-C(O)R$, $RC(O)-C(CH_3)(X)-(CH_2)_n-C(CH_3)(X)-C(O)R$
(in the above formulae, R represents an alkyl, aryl, or aralkyl group containing up to 20 carbon atoms, n represents an integer of 0 to 20; X represents a chlorine, bromine or iodine atom),
$XCH_2-C(O)-CH_2X$, $H_3C-C(H)(X)-C(O)-C(H)(X)-CH_3$, $(H_3C)_2C(X)-C(O)-C(X)(CH_3)_2$, $C_6H_5C(H)(X)-(CH_2)_n-C(H)(X)C_6H_5$
(in the above formulae, X represents a chlorine, bromine or iodine atom; n represents an integer of 0 to 20),
$XCH_2CO_2-(CH_2)_n-OCOCH_2X$, $CH_3C(H)(X)CO_2-(CH_2)_n-OCOC(H)(X)CH_3$, $(CH_3)_2C(X)CO_2-(CH_2)_n-OCOC(X)(CH_3)_2$
(in the above formulae, n represents an integer of 1 to 20),
$XCH_2C(O)C(O)CH_2X$, $CH_3C(H)(X)C(O)C(O)C(H)(X)CH_3$, $(CH_3)_2C(X)C(O)C(O)C(X)(CH_3)_2$, o-, m- or p-$XCH_2CO_2-C_6H_4-OCOCH_2X$, o-, m- or p-$CH_3C(H)(X)CO_2-C_6H_4-OCOC(H)(X)CH_3$, o-, m- or p-$(CH_3)_2C(X)CO_2-C_6H_4-OCOC(X)(CH_3)_2$ o-, m- or p-$XSO_2-C_6H_4-SO_2X$
(in the above formulae, X represents a chlorine, bromine or iodine atom). These compounds can be used each independently or in a combination of two or more thereof.

For the production of a vinyl polymer having a crosslinking silyl group at both molecular chain termini, not only the above-mentioned method using an organohalogen or sulfonyl halide compound having two initiation points as the initiator according to said atom transfer radical polymerization technique but also the method using an organohalogen compound containing a crosslinking silyl group can be used with advantage.

[0072]

The above organohalogen having a crosslinking silyl group

is not particularly restricted but includes compounds represented by the following general formulas (14) and (15), among others.

$R^{15}R^{16}C(X)-R^{17}-R^{18}-C(H)(R^{19})CH_2-[Si(R^1)_{2-b}(Y)_bO]_m-Si(R^2)_{3-a}(Y)_a$ (14)

(wherein R^1, R^2, a, b, m, X and Y are as defined above; R^{15} and R^{16} may be the same or different and each represents a hydrogen atom, an alkyl group containing 1 to 20 carbon atoms, an aryl group containing 6 to 20 carbon atoms or an aralkyl group containing 7 to 20 carbon atoms; R^{15} and R^{16} may be linked to each other at the respective free termini; R^{17} represents-C(O)O-, -C(O)-, or an o-, m- or p-phenylene group; R^{18} represents a direct bond or a bivalent organic group of 1 to 10 carbon atoms which may optionally contain one or more ether linkages; R^{19} represents a hydrogen atom, an alkyl group containing 1 to 10 carbon atoms, an aryl group containing 6 to 10 carbon atoms or an aralkyl group containing 7 to 10 carbon atoms.

$(R^2)_{3-a}(Y)_aSi-[OSi(R^1)_{2-b}(Y)_b]_m-CH_2-C(H)(R^{19})-R^{18}-C(R^{15})(X)-R^{17}-R^{16}$ (15)

(wherein R^1, R^2, R^{15}, R^{16}, R^{17}, R^{18}, R^{19}, a, b, m, X and Y are as defined above)

[0073]

When the "atom transfer radical polymerization" reaction is carried out using the above-mentioned organohalogen having a crosslinking silyl group as the initiator, there is obtained a vinyl polymer having the crosslinking silyl group at one terminus and the highly reactive carbon-halogen bond at the other terminus. By converting the terminal halogen atom of this vinyl polymer to a crosslinking silyl-containing substituent group, for example by the technique described above, there can be obtained a vinyl polymer having the crosslinking silyl group at both molecular chain termini.

[0074]

The above vinyl polymer having crosslinking silyl groups at both termini can also be produced by causing the halogen atoms

of said vinyl polymer to undergo mutual coupling using a compound having at least two same or different functional groups substitutable for the halogen atoms at said termini.

[0075]

The above compound having at least two functional groups, same or different, which are substitutable for the halogen atoms at said termini is not particularly restricted but includes polyols, polyamines, polycarboxylic acids, polythiols and salts thereof; alkali metal sulfides; and so forth.

[0076]

Further, when an organohalogen compound containing an alkenyl group is used as the initiator in said "atom transfer radical polymerization", there is obtained a vinyl polymer having the alkenyl group at one molecular chain terminus and the halogen atom at the other terminus. By converting the terminal halogen atom of this vinyl polymer to an alkenyl group-containing substituent by the technique described hereinbefore, there can be obtained a vinyl polymer having the alkenyl group at both molecular chain termini. By converting these alkenyl groups to crosslinking silyl groups, for example by the technique described hereinbefore, there can be obtained a vinyl polymer having the crosslinking silyl group at both molecular chain termini. While the vinyl polymer having at least one said crosslinking silyl group at the molecular chain terminus may be obtained by an arbitrary combination of the processes described hereinbefore, the following synthetic processes A and B can be mentioned as typical processes.

<u>Synthetic process A</u>

This process comprises

(1) a step of polymerizing a vinyl monomer using an organohalogen compound or a sulfonyl halide compound as the initiator and a transition metal complex as the catalyst by a radical polymerization technique to synthesize a halogen-terminated vinyl polymer,

(2) a step of reacting the halogen-terminated vinyl polymer obtained in the above step (1) with an alkenyl group-containing oxyanion to effect substitution for the halogen and thereby synthesize an alkenyl-terminated vinyl polymer and

(3) a step of adding a hydrosilane compound having a crosslinking silyl group represented by the general formula (1) to the terminal alkenyl group of the alkenyl-terminated vinyl polymer obtained in the above step (2) to effect conversion to a substituent containing said crosslinking silyl group.

Synthetic process B

This process comprises

(1) a step of polymerizing a vinyl monomer by said living radical polymerization technique to prepare a vinyl polymer,

(2) a step of reacting the vinyl polymer obtained in the above step (1) with a compound having at least two sparingly polymerizable (low-polymerizability) alkenyl groups to synthesize an alkenyl-terminated vinyl polymer, and

(3) a step of adding a hydrosilane compound having a crosslinking silyl group represented by the general formula (1) to the terminal alkenyl group of the alkenyl-terminated vinyl polymer obtained in the above step (2) to effect conversion to a substituent containing said crosslinking silyl group.

[High molecular plasticizer for (B) component]

The high molecular plasticizer (B) for use in the invention has a number average molecular weight of 500 to 15000. By adding this high molecular plasticizer, not only the viscosity and slump of the curable composition and the mechanical characteristics, such as tensile strength and elongation, of the cured product obtainable from said composition can be liberally controlled but, compared with the use of a low molecular plasticizer not containing a polymer component in the molecule, the drying properties of the alkyd coat applied to the cured product (i.e. coatability) can be

improved. It is to be understood that the high molecular plasticizer in the invention is not a plasticizer having a group of the above general formula (1).

[0077]

While the number average molecular weight of said high molecular plasticizer is 500 to 15000 as mentioned above, the preferred range is 800 to 10000 and the more preferred range is 1000 to 8000. When the molecular weight is too low, the alkyd coating coatability of the cured product cannot be improved. On the other hand, when the molecular weight is too high, the viscosity is increased to detract from workability.

[0078]

As examples of said high molecular plasticizer, there can be mentioned vinyl polymers obtainable by polymerizing said vinyl monomers by various techniques; polyester plasticizers obtainable from dibasic acids such as sebacic acid, adipic acid, azelaic acid, phthalic acid, etc. and dihydric alcohols such as ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, dipropylene glycol, etc.; polyethers such as polyethylene glycol, polypropylene glycol, polytetramethylene glycol, etc. and derivatives obtainable by converting the hydroxyl groups of such polyether polyols to ester, ether or other groups; polystyrenes such as polystyrene, poly(alpha -methylstyrene), etc.; polybutadiene, polybutene, polyisobutylene, butadiene-acrylonitrile, polychloroprene, and paraffin chloride, among others.

[0079]

Among these high molecular plasticizers, the preferred are plasticizers compatible with the crosslinking silyl group-containing polymer (A). From the standpoint of compatibility, weather resistance and heat resistance, in particular, vinyl polymers are preferred. The preferred, among said vinyl polymers, are (meth)acrylic polymers, with acrylic polymers being particularly preferred. As the mode of synthesizing such polymers, living radical polymerization is

preferred because the method is conducive to a narrow molecular weight distribution and a low viscosity, with the atom transfer radical polymerization technique being particularly preferred.

[0080]

The high molecular plasticizers mentioned above may be used each independently or in a combination of two or more thereof. Where necessary, these plasticizers can be used in combination with low molecular plasticizers within the range not adversely affecting the physical properties.

[0081]

The amount of use of said high molecular plasticizer (B) is 5 to 150 weight parts, preferably 10 to 120 weight parts, more preferably 20 to 100 weight parts, based on 100 weight parts of the vinyl polymer having at least one crosslinking silyl group as (A) component represented by the above general formula (1). At an amount below 5 weight parts, the effect expected of a plasticizer is not expressed. If the amount exceeds 150 weight parts, the mechanical strength of the cured product will not be as high as desired.

[0082]

To the curable composition of the present invention, where necessary, condensation catalysts, fillers, low molecular plasticizers, antisagging agents, colorants, adhesion promoter, aging inhibitors, flame retardants, curability modulators, weather resistance improvers, mechanical characteristics modulators, and the like can be supplemented for adjusting properties of the curable composition or cured product.

[0083]

The condensation catalyst is not particularly restricted, but there may be mentioned various known silanol condensation catalysts, for example, titanic acid esters such as tetrabutyl titanate and tetrapropyl titanate; organotin compounds such as dibutyltin dilaurate, dibutyltin diacetyl acetonate,

dibutyltin maleate, dibutyltin diacetate, dibutyltin dimethoxide, tin octylate and tin naphthenate; lead octylate; amine compounds such as butylamine, octylamine, dibutylamine, monoethanolamine, diethanolamine, triethanolamine, diethylenetriamine, triethylenetetramine, oleylamine, octylamine, cyclohexylamine, benzylamine, diethylaminopropylamine, xylylenediamine, triethylenediamine, guanidine, diphenylguanidine, 2,4,6-tris(dimethylaminomethyl)phenol, morpholine, N-methylmorpholine, and 1,3-diazabicyclo[5.4.6]undecene-7, or these carboxylic acids salts; reaction products or mixtures of amine compounds such as a reaction product or mixture of lauryl amine and tin octylate and organotin compounds; low-molecular-weight polyamide resins obtained from an excess polyamine and a polybasic acid; reaction products from an excess polyamine and an epoxy compound; amino-containing silane coupling agents such as gamma -aminopropyltrimethoxysilane and N- (beta -aminoethyl)-aminopropylmethyldimethoxysilane. These may be used alone or two or more of them may be used in combination. When the hydrolysable group Y is an alkoxy group, the curing rate is comparably slow in the case of the (A) component vinyl polymer alone, thus curing catalysts are preferably used.

[0084]

The filler is not particularly restricted, but there may be mentioned reinforcing fillers such as fumed silica, precipitated silica, silicic anhydride, hydrous silicic, and carbon black; fillers such as calcium carbonate, magnesium carbonate, diatomaceous earth, calcined clay, clay, talc, titanium dioxide, bentonite, organic bentonite, ferric oxide, zinc oxide, activated zinc white and shirasu balloons; and fibrous fillers such as asbestos fibers, glass fibers and filaments and so forth. For obtaining high-strength cured products using such fillers, there can be used a filler selected mainly from among fumed silica, precipitated silica, silicic

anhydride, hydrous silicic acid, carbon black, surface-treated fine calcium carbonate, calcined clay, clay, activated zinc white and so on. When cured products of low strength but high elongation are desired, there can be used a filler selected mainly from among titanium oxide, calcium carbonate, talc, ferric oxide, zinc oxide, shirasu balloons and the like. These fillers may be used singly or two or more of them may be used in admixture.

[0085]

The low molecular plasticizer is not particularly restricted, but there may be mentioned, for example, phthalic acid esters such as dibutyl phthalate, diheptyl phthalate, di(2-ethylhexyl) phthalate and butyl benzyl phthalate; nonaromatic dibasic acid esters such as dioctyl adipate and dioctyl sebacate; polyalkylene glycol esters such as diethylene glycol dibenzoate and triethylene glycol dibenzoate; phosphoric acid esters such as tricresyl phosphate and tributyl phosphate. These may be used alone or two or more of them may be used in combination. It is also possible to incorporate these plasticizers in the stage of polymer production.

[0086]

The antisagging agent is not particularly restricted but includes polyamide waxes; hydrogenated castor oil derivatives; and metal soaps such as calcium stearate, aluminum stearate and barium stearate, among others.

The solid-state modifier is not particularly restricted but includes alkylalkoxysilanes such as methyltrimethoxysilane, dimethyldimethoxysilane, trimethylmethoxysilane and n-propyltrimethoxysilane; alkylisopropenoxysilanes such as dimethyldi-isopropenoxysilane, methyltriisopropenoxysilane and gamma -glycidoxypropylmethyldiisopropenoxysilane, functional group-containing alkoxysilanes such as gamma -glycidoxypropylmethyldimethoxysilane, gamma -glycidoxypropyltrimethoxysilane, vinyltrimethoxysilane,

vinyldimethylmethoxysilane, gamma -aminopropyltrimethoxysilane, N-(beta -aminoethyl)aminopropylmethyldimethoxysilane, gamma mercaptopropyltrimethoxysilane and gamma -mercaptopropylmethyldimethoxysilane; silicone varnishes; and polysiloxanes; among others. By using such a solid-state modifier, it is possible to increase or decrease the hardness or increase the elongation on the occasion of curing of the composition of the invention.

[0087]

The adhesion promoter is not particularly restricted, but there may be mentioned, for example, epoxy resins, phenolic resins, sulfur, various silane coupling agents, alkyl titanates and aromatic polyisocyanates, among others. Using of these can improve adhesion to adherends.

[0088]

The curable composition of the present invention can be prepared as a one-component system such that all the components are premixed and sealed and, after application or installation, let the whole be cured in situ by atmospheric moisture or as a two-component system such that a curing agent comprising the curing catalyst, filler, plasticizer, water, etc. and a polymer composition are admixed prior to application. The curable composition of the present invention can be used for sealing materials, coatings, coating dopes, sealants, adhesives, potting materials, potting compounds, molding compounds, and the like.

[0089]

[Effect of the Invention]

The present invention relates to a curable composition comprising the following two components:

(A) a vinyl polymer having at least one crosslinking silyl group and

(B) a high molecular plasticizer. According to the invention, it becomes easy to coat a curable composition of a vinyl polymer

having a crosslinking silyl group, which has been difficult to be coated with alkyd coatings, with alkyd coatings.

[Document Name] Abstract
[Abstract]
[Subject] To facilitate to coat a curable composition of a vinyl polymer having a crosslinking silyl group, which has been difficult to be coated with alkyd coatings, with alkyd coatings.
[Means for Solving] A curable composition comprising
(A) a vinyl polymer having at least one crosslinking silyl group, and
(B) a high molecular plasticizer is used and cured.
[Selective Figure] none